THE SYSTEM: ANALCITE–LEUCITE–NaCl–KCl–H₂O

AT 300°C AND 300 BARS

by

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Abstract

The system analcite-leucite-NaCl-KCl-H₂O has been studied at 300°C and 300 bars. Three series of experiments were made with respectively 1, 2 and 4 mole/litre total alkali chloride in solution. The average value of $Na/(Na + K)$ in solution when analcite and leucite coexist was found to be 0.377 independent of the total alkali chloride concentration.

Introduction and experimental details

The system analcite-leucite-NaCl-KCl-H₂O has been studied at 300°C and 300 bars with the principal aim of developing an experimental procedure for the study of the chemistry of hydrothermal solutions. This system was chosen partly because it is apparently simple, partly because a recent study of the system (DEBRON 1965) was available. The temperature of 300°C was chosen so that it was in accordance with that used by DEBRON; however, the present study differs from DEBRON's in some details. The amount of material has been reduced to approximately 1/10th of that used by DERBON, so that 36 individual experiments could be made simultaneously in one run, while DEBRON made one experiment per run. Three series of experiments were made with respectively 1, 2 and 4 mole/litre total alkali chloride in solution at 25°C and 1 atm., while DEBRON's experiments were made with varying total alkali chloride concentrations.

Procedure

Approximately 20 mg analcite, crushed to between 100 and 150 mesh, was weighed into a 5 cm long silver capsule and 0.2 ml alkali chloride solution was pipetted into the capsule. The solution occupied 75 % of the volume of the capsule. The use of brass jaws on the vice holding the capsule prevented boiling of the solution during welding, since this metal conducts the excess heat away rapidly. The sealed capsules were placed in a Morey-type closed bomb (total volume = 97.6 ml) and distilled water was added so that it made up 75% of the volume remaining. According to KENNEDY (1950) the specific gravity of water is 0.75117 at 300°C and 300 bars.

After 283 hours at 300°C the run was stopped and the solutions analysed for Na and K by flame photometry and for Cl by potentiometric titration. All the solid phases were examined under the microscope and some samples by means of Guinier X-ray technique. Of a total of 42 capsules (including blank and standards) only one (no 25') was shown to have leaked.

Analcite from an unknown locality (weakly birefringent, $n_0 = 1.487$, $a_0 = 13.715$ Å; Na₂O 12.3 %, K₂O 1.00 % and CaO 0.00 %) was used as starting material. The solutions were made from NaCl and KCl of analytical grade manufactured by E. MERCK and from distilled and deionised water.

Results

The amounts of Na and K in the solid phases after the run were calculated by subtracting the amount found in the solution by chemical analysis from the amount originally added as analcite and in solution. In Table I the values of $X_{Na} = Na/(Na+K)$ in the solutions and solid phases are tabulated. According to Guinier X-ray films and the microscopic examinations the solid phases after the experiments consisted of analcite, analcite + leucite, and leucite; no other solid phases were observed. The cell edges, determined by the method of least squares using the same reflections from all films, are compared with the composition of the analcites in Table II. It is seen that the cell edge of analcite decreases with increasing potassium content. This has also been found by Peters et al. (1966).

Table I

No.	$(X_{Na\ solid})$	$(X_{Na\ solid})$	Solid phases
1 mole/1:			
11	0.99_1	0.95	anal.
11'	0.99_8	0.99	,,
12	0.62_1	0.91	,,
12'	0.61_6	0.93	,,
13	0.36_2	0.86	,,
13'	0.34_8	0.84	,,
14	0.38_9	0.60	anal. + leuc.
14'	0.38_1	0.63	,, + ,,
15	0.38_4	0.28	,, + ,,
15'	0.37_3	0.36	,, + ,,
16	0.37_5	0.17	leuc.
16'	0.37_6	0.08	,,
2 moles/1:			
21	0.99_9	0.97	anal.
21'	0.99_9	0.97	,,
22	0.60_9	0.93	,,
22'	0.62_6	0.86	,,
23	0.37_0	0.62	anal. + leuc.
23'	0.37_6	0.55	,, + ,,
24	0.36_9	0.25	,, + ,,
24'	0.36_1	0.18	,, + ,,
25	0.31_3	0.002	leuc.
26	0.21_1	0.06	,,
26'	0.24_3	0.03	,,
4 moles/1:			
41	0.99_6	1.0	anal.
41'	0.99_6	1.0	,,
42	0.61_1	0.86	,,
42'	0.60_7	0.89	,,
43	0.37_5	0.25	anal. + leuc.
43'	0.38_8	0.23	,, + ,,
44	0.29_1	0.01	leuc.
44'	0.31_1	0.	,,
45	0.18_6	0.03	,,
45'	0.23_1	0.01	,,
46	0.11_9	0.	,,
46'	0.12_2	0.	,,

Table II

Composition and cell edge of analcite.

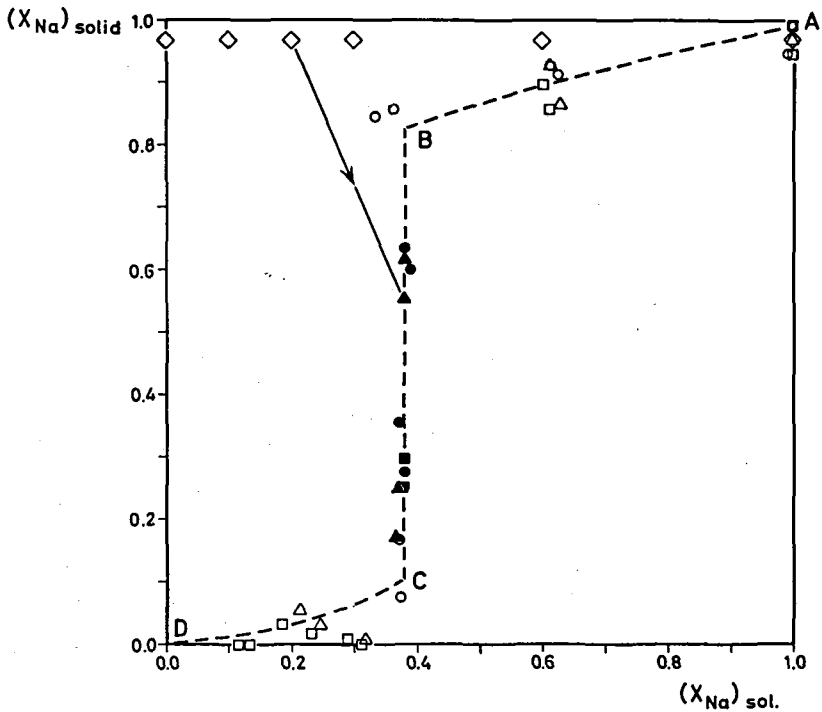| No.	a_0 (Å)	K mole %	Remarks
I	13.714	0	result from a preliminary study
start	13.715	3.5	
11	13.710	5.5	
12	13.707	8.9	
13	13.705	14.4	
14	13.705	15.5	2 solid phases
15	13.702	15.5	2 solid phases

Fig. 1

The relations between X_{Na} in solution and solid phases.

    Diamonds : starting compositions
    Circles   : 1 mole/liter alkali chloride in the solutions
    Triangles : 2 – ” –   ”   ”   ” ”   ”
    Squares   : 4 – ” –   ”   ”   ” ”   ”

Open circles, triangles, and squares indicate one solid phase (analcite in the region A–B and leucite in C–D) after experiment. Solid circles, triangles, and squares indicate coexistence of analcite and leucite.

The arrow shows the path followed during the experiment no. 24′.

Discussion

The results have been plotted as a function of X_{Na} in solution and solid phase respectively (Fig. 1). The points are grouped close to a curve consisting of three parts: AB, BC, and CD. AB and CD represent distribution equilibria of Na and K between solution and analcite, and solution and leucite respectively. BC represents a three-phase system consisting of analcite of composition B, leucite of composition C, and solution of a composition given by the abscissa of BC.

Accordingly, the following three reactions have been examined:

1) Na-analcite + KCl   = K-analcite + NaCl
2) analcite + KCl   = leucite + NaCl
3) K-leucite + NaCl   = Na-leucite + KCl

As seen in Fig. 1, reaction 2) is uninfluenced by variations in the total concentration of alkali chloride. The position of the equilibrium can therefore be expressed by the mole ratio of sodium in solution. If it can be assumed that the difference between the pressure used in the run (300 bars) and that used by DEBRON (96 bars) is not critical, then a comparison can be made between the two sets of results. The average value of $(X_{Na})_{sol.}$ when analcite and leucite coexist found by DEBRON was 0.394 with a standard deviation s = 0.03 (11 determinations). The corresponding results in this study are 0.377, s = 0.008 (10 determinations). DEBRON used mainly leucite as starting material. The agreement between the two sets of results indicates that equilibrium has been reached.

Conclusion

If it is assumed that equilibrium has been reached in all experiments (13 and 13' excluded) the points for reactions 1) and 3) should lie on smooth curves. The scatter found is probably due to the inaccuracy involved in the determination of the solid phases. Accordingly the experimental procedure described is not suited for examination of reactions where the composition of the solid phase varies (as in reactions 1 and 3 above). Chemical analyses of the solid phases would improve the method considerably when the composition of the solid phase varies. However, the method appears to yield satisfactory results when the equilibrium constant can be expressed by the concentrations of the components in solution.

References

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